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THE DEVELOPMENT OF A YELLOW  
GLAZE FOR TERRA COTTA

BY

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THESIS

FOR THE

DEGREE OF BACHELOR OF SCIENCE

IN


CERAMIC ENGINEERING

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COLLEGE OF ENGINEERING

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

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ENTITLED " The Development of a Yellow Glaze for Terra Cotta"

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

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# The Development of a Yellow Glaze for Terra Cotta

## Part One

### I

#### Introduction

In developing a yellow glaze for terra cotta there are three things to consider.

A glaze for such use must mature well at the cone to which terra cotta ware is burned, which is usually about Seger cone five (5). It must develop the desired gloss and be free from crazing, pinholing, feathering and all glaze defects at this cone.

The glaze to be useful as a terra cotta glaze, must be such that it will mature properly, without defects, when applied on a green terra cotta body over a slip which has been previously applied. A terra cotta clay mix does not burn to a white, and because of this it is necessary to use a white opaque slip between the glaze and the body so that the color of the body will have no effect on the glaze colors.

The use of the coloring oxide is very important. The coloring oxide should be such that it will produce good yellows which are clear and of such a strength that a series of shades may be obtained by variations in the amount of the coloring oxide used. The coloring strength of the oxide has a bearing on the practicability of its use commercially, for if excessive amounts have to be used to produce the desired depth of color in the glaze it may not be economically practical to use it as a pigment substance.

Summarizing, my objects of research are:



1. To develop a glaze which was suitable for use at Cone five (5) together with a slip on a green body.

2. To secure a combination of glaze and coloring oxide to produce a yellow which would be satisfactory from the color standpoint and be economically suitable for use as a glaze for terra cotta ware.



### Discussion of Previous Work and Literature.

There seems to be pretty close agreement as to the yellow-producing oxides and pigment materials in the various authoritative books on the subject of glazes and ceramic colors. The range of materials for the production of yellow colors in glazes, as obtained from the various sources includes uranium oxide, iron oxide, antimony oxide, titanin oxide, leukonin, (sodium antimonate) tungstic acid, molybdic oxide, and a coloring frit made up of uranic nitrate fritted with feldspar. The various references and subject matter from them are as follows:

1. R. Hainbach- "Pottery Decorating".

According to Hainbach, very handsome pure yellows are obtained by the use of antimonin oxide in a white glaze in the proportions of five to ten per cent (5-10%) oxide and ninety to ninety-five per cent (90-95%) glaze. He also states that ferric oxide and uranium oxide develop yellows, the ferric oxide also being used with antimony oxide for procuring reddish or brownish red yellows. He is also the authority for the statement that very handsome yellows have been obtained with silver, but this, obviously, is too expensive a material for use as a coloring oxide in a terra cotta glaze.

2. A. B. Searle- " Ceramics Industries Pocket Book".

In his list of "colors used in pottery, glazing, enamelling and glass-staining", Searle lists the oxides of titanium, antimony, iron and uranium as being yellow-producing oxides.





### 3. Emile Bourry- "Treatise on Ceramics Industries".

Bourry states that the oxide of uranium gives a yellow in an oxidizing fire. He also states that titanitic acid develops yellows. To use his words; "In glazes it (titanic acid) gives only yellow tints, due, partly at least, to the iron that raw titanitic acid always contains in commerce." He is authority for the statement that pure iron oxide develops a good yellow, although it tends toward a brown at high temperatures. He lists uranium oxide as a good yellow-producing oxide, except in the presence of lead, where it turns to an orange.

### 4. Taxile Doat- "Grand Feu Ceramics".

the authority for the use of nitrate of uranium fritted with feldspar as producing yellows is found here. Doat also advocates the use of uranium oxide for yellows, as well as oxide of iron for slightly brownish yellows.

### 5. Chemical Abstracts, XI, 93; "A New Yellow Color"- Anon.

According to this article, cerium phosphates have been used to develop brilliant yellows.

### 6. Notes on Ceramics 6.

I found in my Ceramics notes a statement as to the use of tungstic acid\* and molybdic oxide in the presence of manganese for the development of yellow glazes.

### 7. Report of German Ceramic Society, Dr. Funk.

Reference was made in this report to the use of cerium oxide for the development of yellow glazes, no authority being given for the statement.

\*. Hertwig, Sprechsaal, 49: 1845-1846 (1903). Abstract in the





Jour. Soc. Chem. Ind. Jan. 30 (1904) pg. In a reducing fire yellow and orange shades with the use of tungstic acid.

8. Hertwig-Sprechsaal 49; p.120.

Cerium phosphate is used for the development of brilliant yellows, according to this authority.

9.. Hermann A. Seger, Collected Writings.

Seger uses titanio acid in the development of brilliant yellows in underglaze colors at low temperatures. He makes the statement that the yellow color may be due to the presence of iron as an impurity.

Uranium is also used by Seger for the development of lemon yellows. With the use of uranium the necessity of avoiding reducing conditions becomes paramount.

10. Frank H. Riddle, "The Coloring Power of Uranium Oxide in Glazes of Various Compositions. T.A.C.S., Vol. 8.

The statement is made that the coloring power of uranium oxide is very great, as little as .006 equivalents producing a decided yellow.

11. Earl T. Montgomery- "Study of Underglaze Colors with View of Determing the Most Insoluble and Non-Volatile Underglaze Color Composition. T.A.C.S. Vol. 13.

Montgomery finds that yellowish grays, yellowish blacks and yellowish greens are developed with uranium oxide. The color was prepared as a frit. The higher members gave the colors noted above. There is no reference in this to there being any reducing conditions in the burn.



## III

## Experimental Method Employed.

The method of procedure in the work consisted of the following steps:

(a) Selection of a body material which would closely approximate the body actually used in commercial body as to general behaviour.

(b) Selection of a suitable white slip for use in masking the color of the body, being used for application on the green body.

(c) Selection of a glaze suitable for application over the white slip on the green body.

(d) Consideration and investigation of the coloring oxides which are thought to be, and have been reported to be yellow-producing oxides, together with a consideration of the proper proportions necessary for incorporation with the glaze to produce satisfactory shades of yellows.



## IV

## Body, Slips and Glazes Investigated.

1. Body. The body used was made of Bloomingdale Stoneware clay. Preparation of the body consisted of grinding in a wet pan and forming briquettes about three-fourths of an inch thick and two inches wide by four inches long. These were formed in a small brick auger machine by the use of a suitable die, the column run out being cut to the desired width of pieces. These were air dried and then dried in a steam-heated rack drier.

2. Slips. The slips used were a typical terra cotta slip and a vitreous white slip as follows:

## (a) Terra cotta slip

English China clay	15%
Tennessee Ball clay	10%
Feldspar	50%
Flint	25%

## (b) Vitreous white slip

Cornwall stone	40%
English Ball clay	18%
English China clay	20%
Boric Acid	2%
Flint	15%
Calcium Carbonate	2%
Barium Carbonate	2%
Magnesium Oxide	1%

The preparation was the same for both slips and consisted merely of grinding wet for three hours in ball mills and lawning through a screen of 140 meshes to the inch.



3. Glazes used. Two glazes were used, a fritted glaze and a bristol glaze:

(a) Fritted Glaze:

Fritt:--

Whiting 35 parts

Feldspar 56 parts

Borax 57 parts

Flint 54 parts

Boracic acid 1 part

Ceramic Formula:

.3 PbO

.35 CaO    .283 Al<sub>2</sub> O<sub>3</sub>    3.0 SiO<sub>2</sub>

.2 K<sub>2</sub>O    .31 B<sub>2</sub>O<sub>3</sub>

.15 Na<sub>2</sub>O

Glaze :-

Fritt 160 parts

White lead 77 parts

Feldspar 56 parts

China clay 21 parts

Flint 44 parts

(b) Bristol Glaze:

Ceramic Formula:

.270K<sub>2</sub>O

.234 ZnO

.396 CaO    .55 Al<sub>2</sub> O<sub>3</sub>    3.3 SiO<sub>2</sub>

.100 BaO

Batch weights, figured on the basis that the coloring oxides replace like amounts of CaO.

Extreme .005

150.2 Feldspar

18.9 Zinc Oxide

39.1 Calcium Carbonate

19.7 Barium Carbonate

51.6 Raw clay





17.9 Calcined clay

67.1 Flint

(.005 Equivalents of coloring oxide).

Extreme .10

150.2 Feldspar

18.9 Zinc Oxide

29.6 Calcium Carbonate

19.7 Barium Carbonate

51.6 Raw Clay

17.9 Calcined Clay

67.1 Flint

(.10 equivalent of coloring oxide).

#### 4. Biscuited Tile Trial Pieces.

Trial pieces of biscuited tile with the application of glaze on them were run to assure a knowledge of the various colors developed, in case the green pieces should not develop properly.

#### 5. Oxides used and their source

(a) Leukonin ( $2\text{Na}_2\text{SbO}_3 \cdot 7\text{H}_2\text{O}$ ) Introduced as such.

(b) Cerium oxide ( $\text{CeO}_2$ ) Prepared by igniting basic ceric nitrate strongly.

(c) Ferrous oxide ( $\text{FeO}$ ) Introduced as ferric oxide ( $\text{Fe}_2\text{O}_3$ ), pure.

(d) Uranium oxide ( $\text{U}_2\text{O}_3$ ) Introduced as sodium uranate ( $\text{Na}_2\text{U}_3\text{O}_6 \cdot \text{H}_2\text{O}$ )

(e) Tungstic acid ( $\text{H}_2\text{WO}_4$ ) Introduced as such.

(f) Molybdic oxide ( $\text{MoO}_3$ ) Introduced as such.

(g) Uranium Nitrate ( $\text{U}(\text{NO}_3)_3$ ) Introduced as such.

(h) Manganese dioxide ( $\text{MnO}_2$ ) Introduced as such.



(i) Titanic oxide ( $\text{TiO}_2$ ) Introduced as such.



## Blending, Dipping and Firing.

## 1. Blending.

In both the fritted and the bristol glaze the two color extremes, .005 equivalents and .10 equivalents of color oxide present, were prepared and the intermediate colors prepared by blending these extremes in the proper proportions figured in dry weight of glaze. All blending was carried out on the basis of the weight of dry glaze present in the glaze mix. This was found by weighing a certain known amount out in a dish, drying the glaze, weighing again and calculating the weight of dry material in one gram of wet material from the data obtained.

## Sample Calculation for Blending.

## (a) Determination of dry weight.

## 1. Extreme .005 equivalents coloring oxide.

Weight of beaker and glaze slip -147.5 gm.

" " " and glaze slip dried 141.1gm.

" " " alone 136.1gm.

Weight of slip 147.5-136.1 11.4 gm.

" " " dried 141.1 136.1 5.0 gm.

Then 1 gm. dry  $\frac{11.4}{5}$  2.28 gm. wet glaze slip.

## 2. Extreme .10, calculated similarly, gives:

1 gm. dry 2.71 gm. wet glaze slip.

3. The method of blending is by the position of the glaze desired in reference to the two extremes as shown below.



It will be noted that glaze .04 for instance, is seven (7) divisions from extreme .005 and twelve (12)



divisions. The calculations , then, for making up the glaze are as follows:

50 x 12/19 x 2.28      72.0 gm. (.005 extreme)

50 x 7/19 x 2.71      49.9 gm. (.10 extreme)

## 2. Dipping.

Both the slips and the glazes were dipped. The slip was brought to a specific gravity of approximately 1.5 as this is the most workable weight for dipping. The glazes were applied by dipping after the slips were dipped, the specific gravity being the same as the slips when pieces were dipped.

## 3. Firing.

The burning was all done in one burn, that is, the body, slip and glaze were all burned at one burn. The Time Temperature Schedule for the burn is shown in Graph No. 1. Care was exercised to have an oxidizing atmosphere in the kiln at all times, and ample time was allowed at the end of the burn for the purpose of "soaking", or equalizing the temperature over the entire kiln. Cones four and six were placed in the saggars to indicate the heat treatment and cones three, four, five and six were used as sight cones.

The burn went to Seger cone 5.





## Results.

## 1. General.

(a) The sight cone 5 was well down and the cones in the saggars indicated that the cone 5 heat treatment extended to all parts of the kiln.

(b) Fitting of glaze, slip and body.

The results of the Bloomingdale Stoneware pieces showed that the method of dipping was probably at fault, as the glazes and slips rolled and beaded considerably.

(c) Biscuited tile trials.

The glazes all developed well on the biscuited tile and the tabulated results as to color were obtained from these trials.



Table No. 1

Equivalents of Coloring Oxide employed

Color Oxide	.005	.01	.02	.04	.07	.10
1 $U_2O_3$	Trace	Slight	Fair	Good yellow	Muddy Brown	Almost Black
2 $TiO_2$	None	None	None	None	None	None
3 $2Na_2SbO_3 \cdot 7H_2O$	None	None	None	None	Trace	Slight
4 $CeO_2$	None	None	None	None	Trace	Slight
5 *FeO (Ba)	Trace	Slight	Slight	Fair Light Brownish	Almost muddy	Muddy
6 †FeO (Mg)	"	"	"	"	"	"
7 $2NaSbO_3 \cdot 7H_2O$	None	None	None	None	None	None
8 $U_2O_3$	Trace	Slight	Fair	Good Yellow	Muddy	Almost Black
9 $TiO_2$	None	None	None	Trace	Trace	Slight Brown Yellow
10 $Fe_2O_3$	Trace	Trace	Slight	Pale Brown	Pale Brown	Pale Grayish yellow
11 $CeO_2$	None	None	None	Trace	Cream	Cream

\* FeO in the original Bristol glaze, with .1 equivalent barium oxide.

† FeO in the original Bristol glaze, except that .1 equivalent magnesium oxide replaces the barium oxide.

Nos. 1 - 6 inclusive Bristol Glaze.

Nos. 7 - 11 inclusive Fritted Glaze.



## VII

## Conclusions.

1. From the results of the Bloomingdale Stoneware trials there is obviously something wrong with the applications of the glaze and slip on the body. The writer has had similar experiences with attempts to dip Bristol glazes on this same body which were corrected by spraying the glaze on. A better application could no doubt have been made by spraying.
2. The glazes on the tile trials were well matured, showing that the glazes are suitable for maturity at this temperature.
3. Of the two glazes the Bristol appears to have an advantage over the fritted glaze for application to the green pieces, as they, in general adhered better on the green pieces than the fritted glazes.
4. Coloring Oxides.

Of the coloring oxides employed, only uranium and iron oxides appear to be worth while as a commercially practicable coloring constituent. The higher members of the Uranium series show up gray which is, no doubt, due to the excessive amounts used. Iron develops a fair yellow, but one that is rather indistinct and slightly muddy.



## Part Two

## I

## Changes in Glaze Composition.

It appears that the Bristol glaze behaves better than the fritted glaze on green bodies as the Bristol glaze was adopted as the standard.

The R. O. members of the glaze were varied somewhat to determine what effect, if any, this would have on the color oxides. The two variations are as follows:

## "X" Bristol

.333  $K_2O$

.334 CaO      0.55  $Al_2O_3$       3.3  $SiO_2$

.333 YnO

## "Y" Bristol

.350  $K_2O$

.317 CaO      0.55  $Al_2O_3$       3.3  $SiO_2$

.333 YnO

The oxides were used to replace equivalent amounts of calcium oxide, as in Part One.

Two other oxides were employed in this burn, which were not available for use in the first burn, namely tungstic acid, and molybdic oxide. These were used both alone and in the presence of .05 equivalents of manganese dioxide.





Preparation, Blending, Application, Firing.

1. The preparation of the glazes was the same as outlined under Part One.
2. Blending has already been outlined in Part One, the same method being employed in this burn.
3. Application.

The method of application was different from that employed in Part one. Instead of dipping, both the slip and the glaze were applied by spraying, which gave a good even coat, without showing any drying cracks.

4. Firing.

The firing schedule was the same as that employed in the first burn, the sight cones and the Seger cones being the same and the burn going to the same cone--Cone 5.

The writer could observe no indications of reducing conditions in the kiln. Care was exercised to avoid forcing the fires. The cones indicated a good even cone 5 heat all over the kiln with the exception of two saggars in the bottom, when it was estimated the heat was cones three and four respectively.



## III.

## Results.

## 1. Application.

The application of the glaze on the green body was rather thin, but it was thick enough to indicate that the body, slip and glaze were well fitted at this cone (Segger cone 5). The majority of the glazes indicated that they would mature at this cone, as is shown in Table No.2.

## 2. Comparison of the slips.

Of the two slips, the vitreous slip lends itself most readily to the proper maturing of body, slip and glaze at cone 5.

## 3. Effect of absence of Barium on the iron oxide yellows.

A decided difference in the tone of the iron oxide yellows is shown in the absence of barium oxide from the RO members of the glaze, the ones without barium present being much more clear and uniform and avoiding the muddy appearance altogether.



Table No.2.

## Data on the Maturity of the Glazes.

Amount of oxide used	.005	.01	.02	.04	.07	.10
"X" Bristol:						
$U_2O_3$	0	x	x	x	0	0
$Fe_2O_3$	x	0	x	x	x	x
$H_2WO_4$	x	x	x	x	x	x
$MoO_3$	x	x	x	x	x	x
"Y" Bristol:						
$U_2O_3$	x	x	0	0	x	0
$Fe_2O_3$	x	x	0	0	0	0
$H_2WO_4$	x	x	x	x	x	x
$MoO_3$	0	0	0	0	x	0
Original Bristol:						
$MoO_3$	x	x	x	x	x	x
$H_2WO_4$	0	0	0	x	x	0
" & $MnO_2$	x	x	x	x	x	x
$MoO_3$ & $MnO_2$	x	x	x	x	x	x
$U(NO_3)_3$ & Feldspar Pritt	0	0	x	x	0	0

0- indicates glazes not matured.

x- indicates glazes which matured.



Table No. 3  
Colors Obtained

Coloring Oxide	.005 eg.	01 eg.	.02 eg.	.04 eg.	.07eg.	.10eg.
<u>"X"</u>						
<u>Bristol</u>						
$U_2O_3$	Trace	Slight	Pale	Muddy	Gray	Almost Black
$Fe_2O_3$	Trace	Trace	Slight	Fair	good buff tinted yellow	good yellow slightly buff
$H_2WO_4$	None	None	None	None	None	None
$MoO_3$	None	None	None	None	None	None
<u>"Y"</u>						
<u>Bristol</u>						
$U_2O_3$	Trace	Slight	Pale	Muddy	Gray	Almost Black
$Fe O$	Trace	Trace	Slight	Fair	Good buff tinted yellow	good yellow slightly buff
$H_2WO_4$	None	None	None	None	None	None
$MoO_3$	None	None	None	None	None	None
<u>Original Bristol</u>						
$MoO_3$	None	None	None	Trace	Slight pale brown	Slight pale brown
$H_2WO_4$	None	None	None	None	None	None
$H_2WO_4 \& MnO_2$	Light brown	Light brown	Light brown	Light brown	Light brown	Light brown
$MoO_3 \& MnO_2$	Light brown	Light brown	Light brown	Light brown	Light brown	Light brown
$U(NO_3)_3$	Slight	Slight	Light	Fair	Good	Blackish





# TIME-TEMPERATURE CURVE

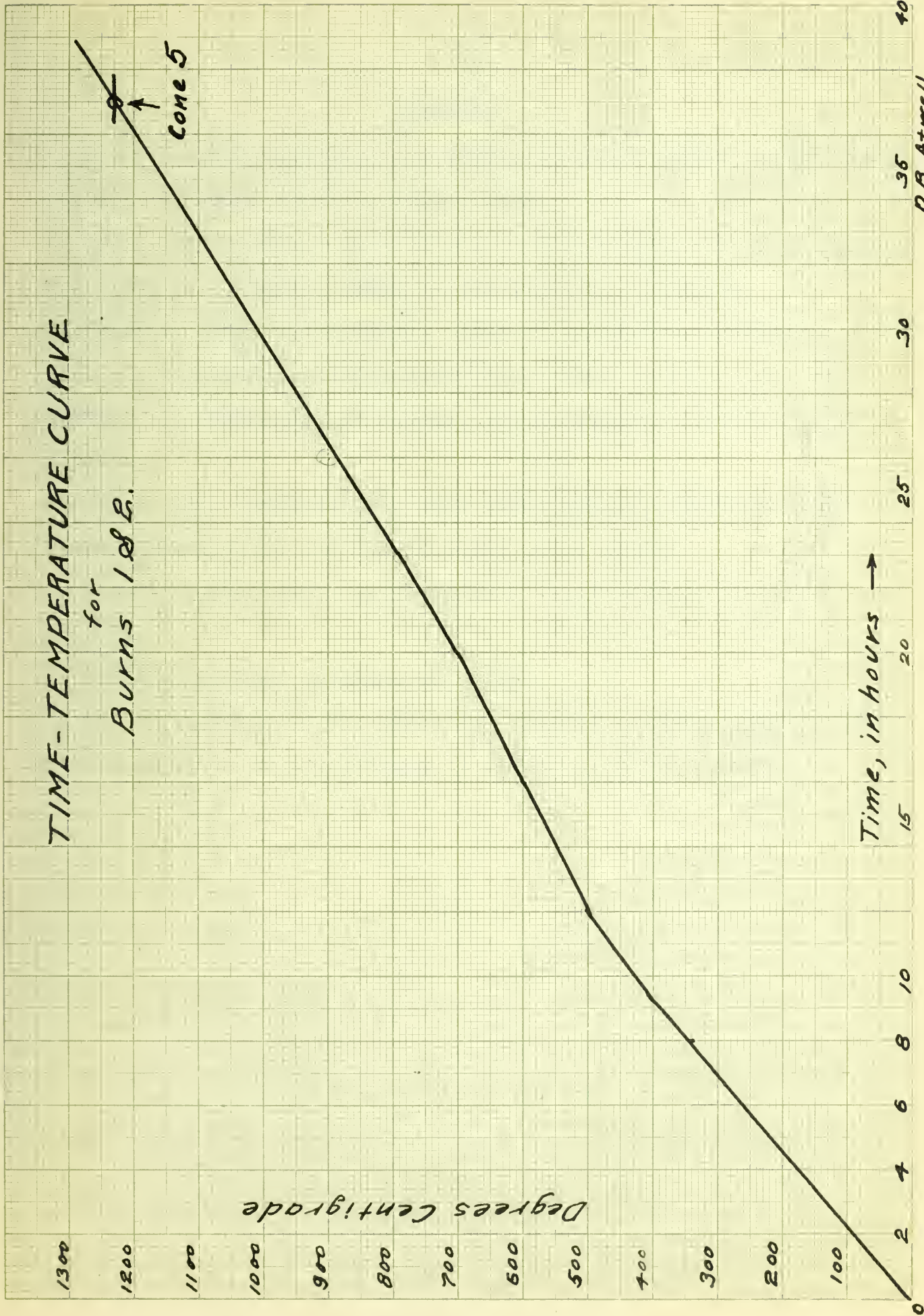
for  
Burns 1 & 2.

Cone 5

Degrees Centigrade

Time, in hours →

D.B. Atwell





## IV.

## Summary.

1. Uranium oxide develops good shades of lemon yellow, except where too much is used, where it turns black.
2. Iron oxide develops good colors of yellow-buff. The iron yellows are, however, slightly muddy in the presence of barium.
3. Tungstic oxide and molybdic oxide of themselves develop no color. With .05 equivalents of manganese dioxide they develop light buff browns. The manganese, of course, predominates in producing this color.
4. Ceric oxide produces only very faint yellows, which are, of course, impracticql for use in terra cotta glazes.
5. Titanic oxide, also, develops only faint colors, which are useless.
6. Leukonin as used develops no color.
7. The application of the glaze and slip by spraying leads to the best results as to the fitting of the body, glaze and slip.





### Conclusions.

The Uranium oxide color is the best true yellow of those used here. Uranyl nitrate fritted with feldspar gives a good clear lemon yellow, which is very promising in appearance.

The "X" and "Y" Bristol glazes show no improvement over the original Bristol except in the case of iron, which has already been noted. The one which, in my opinion, is best for use is the "X" Bristol, because of its conformity to the typical Bristol RO formula and because it develops a fine gloss and allows of considerable variation to allow for fitting it to any body on which it is used.

Iron oxide colors are very good, especially where a yellow with a slightly buff tinge is desired. The advantage of iron oxide is its cheapness and availability and comparative purity with which it can be obtained.

The tungstic and molybdic oxide glazes with manganese are not true yellows at all. Their use as such is therefore impossible.

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